Title	Vapor Phase Catalytic Condensation of Furfural and Acetaldehyde
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(b) The band in pure metal was separated into $m+1$ pieces in alloy, and the total number of surface states was either $m+2$ or 2.

(c) An attempt of introducing the concept of the surface state into the explanation of activated adsorption had already been made by the authors (Ist ann. meet., Chem. Soc. Japan (May 3, 1948)). Considering above results (a) from this standpoint, it may be able to conclude that the change of catalytic activity in alloys depends much upon the various irregularities at the surface, and little upon the "interior" composition.

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24. Vapor Phase Catalytic Condensation of Furfural and Acetaldehyde

Ken-ichi Fukui and *Masakazu Takei*

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Vapor phase condensation of furfural with acetaldehyde in the presence of several basic catalysts were investigated for the purpose of obtaining furfuracrolein.

Using MgO catalyst under the suitable condition, we could obtain furfuracrolein with 70.5% yield for theoretical: some experimental results are tabulated in following 3 tables, where the mol ratio of acetaldehyde to furfural is 1.3. The influence of the mol ratio in charge was also investigated, and the result indicated that in general the yield was larger when furfural was used in excess.

Tab. 1. Comparison of various catalysts.
(350°C: contact time: 24.5 sec)

Catalyst	F・A	R	A/F	k_1/k_2
MgO	0.705	0.047	1.55	2.30
ZnO	0.553	0.033	1.29	1.23
CaO	0.360	0.259	4.14	0.57
K_2CO_3	0.256	0.314	1.31	0.34

F・A: (mol furfuracrolein produced/mol fulfural converted)
R: (g resinous matter produced/g total aldehyde used)
A/F: (mol ratio of acetaldehyde to furfural which was converted to resinous matter)
k_1/k_2: (ratio of rate constant of desired reaction to that of resin formation reaction)

Tab. 2. Influence of temperature.
(Catalyst: MgO; Contact time: 24.5 sec)

Temp. °C	F・A	R	A/F	k_1/k_2
250	0.558	0.047	1.84	1.26
300	0.484	0.126	1.85	0.95
350	0.482	0.104	1.19	0.94
400	0.464	0.082	0.97	0.84

Tab. 3. Influence of contact time.
(Catalyst: MgO; Reaction temp.: 350°C)

Time sec.	F・A	R	A/F	k_1/k_2
18	0.500	0.074	1.13	1.04
24.5	0.482	0.104	1.19	0.94
39	0.400	0.137	0.77	0.68

25. Studies on the Rate of Reaction CH_4 and CO_2. (III)

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The rate of thermal reaction of CH_4 and CO_2 was investigated at 1147−1236°K and 100−300 mmHg in which the pressure change caused by the reaction was determined and the reaction product was analysed with a modified Ambler's apparatus.

In the earlier stage of the reaction, H_2 is mainly formed, as the result of a mere decomposition of CH_4 and in the laler stage CO is formed due to the reaction of CO_2 and H_2 which increased rapidly as the reaction proceeds, but the amounts of CO are always smaller than those of H_2.

At constant intial pressures of CH_4, the amounts of H_2 produced are scarecely affected by the initial pressures of CO_2, but contrarily those of CO change regularly with the initial CO_2 pressure. On the other hand, both amounts of H_2 and CO increase conspicuously with the initial CH_4 pressure when the initial pressures of CO_2 are constant.

In the earlier stage of the reaction, the rate of pressure change is the 1st order with respect to the partial pressure of CH_4, while the rate of CO formation is always approximately 1st order respecting partial pressure of CO_2.

On the basis of the results of these experiments and the previous investigations on the rates of the reaction of $CO_2+H_2=CO+H_2O$ and $C+CO_2=2CO$, the following mechanism is proposed:

$$CH_4 \xrightarrow{k_1} C\ (ad)+2H_2$$

$$CO_2 \underset{r_2}{\overset{k_2}{\rightleftarrows}} CO_2(ad)$$

$$CO_2(ad)+H_2 \xrightarrow{k_3} CO+H_2O(ad)$$

$$C(ad)+H_2O(ad) \xrightarrow{k_4} CO+H_2$$